

# Impurities and orbital dependent superconductivity in $\text{Sr}_2\text{RuO}_4$

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There now exists a wealth of experimental evidence that  $\text{Sr}_2\text{RuO}_4$  is an odd-parity superconductor. Experiments further indicate that among the bands stemming from the Ru  $\{xy, xz, yz\}$  orbitals, the portion of the Fermi surface arising from the  $xy$  orbitals exhibits a much larger gap than the portions of the Fermi surface arising from the  $\{xz, yz\}$  orbitals. In this paper the role of impurities on such an orbital dependent superconducting state is examined within the Born approximation. In contrast to expected results for a nodeless  $p$ -wave superconductor the unique nature of the superconducting state in  $\text{Sr}_2\text{RuO}_4$  implies that a low concentration of impurities strongly influences the low temperature behavior.

74.20.Mn, 74.25.Bt, 74.25.Jb

Since the discovery of superconductivity in the layered oxide  $\text{Sr}_2\text{RuO}_4$  in 1994 [1] and the prediction of odd-parity superconductivity [2] it has been quickly established that the symmetry of the superconducting order parameter is indeed of odd parity. Early NQR [3], tunneling [4], and impurity studies [5] clearly indicated that  $\text{Sr}_2\text{RuO}_4$  is not a conventional superconductor. More recently  $\mu\text{Sr}$  measurements reveal that the superconducting state breaks time reversal symmetry [6] and Knight shift measurements show no change in the spin susceptibility when passing through the superconducting transition [7]. These measurements indicate that the superconducting state is described by a spin-triplet pair amplitude with an orbital dependence  $\eta_1 k_x + \eta_2 k_y$  where  $(\eta_1, \eta_2) \propto (1, i)$  when no magnetic field is applied. Such a superconducting state is nodeless in a quasi-2D material. The effect of impurities within the Born approximation on a nodeless  $p$ -wave state has been well studied [8,9]. The results indicate that impurities do not drastically change the low temperature properties of the superconducting state unless a sufficiently large impurity concentration is present. For  $\text{Sr}_2\text{RuO}_4$  the experiments of Nishizaki *et al.* indicate that impurities strongly alter the low temperature properties even in the small impurity concentration limit [10]. This has previously been interpreted as an indication that  $\text{Sr}_2\text{RuO}_4$  is in the unitarity scattering limit [11]. Here it is shown that the Born approximation can explain the experimental results once the unique microscopic (orbital dependent) nature of the superconducting state in  $\text{Sr}_2\text{RuO}_4$  is considered.

The superconducting state described above is fully gapped so it is difficult to understand the experimental observation that only approximately half of the Fermi surface exhibited an energy gap [10]. It was suggested that this feature can be understood when the highly planar character and the electronic structure of the Ru ions are considered [12]. The formal valence is  $\text{Ru}^{4+}$  which implies that the electronic properties are due to four electrons in bands described by Wannier functions with Ru  $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$  orbital character. The quasi-2D nature of the electronic dispersion and the different parity under the reflection symmetry  $\sigma_z$  ( $z \rightarrow -z$ ) of the  $xy$  and the  $\{xz, yz\}$  Wannier functions implies that the bands are derived from either the  $xy$  or the  $\{xz, yz\}$  Wannier functions (strictly speaking this is correct only in the 2D limit). The parity difference under  $\sigma_z$  further inhibits Cooper pair scattering between the  $xy$  and the  $\{xz, yz\}$  bands [12]. Consequently, the superconductivity in the  $xy$  and the  $\{xz, yz\}$  bands can be considered as nearly independent and to a first approximation the specific heat data can be understood as the appearance of superconductivity in either the  $xy$  sheet or the  $\{xz, yz\}$  sheets of the Fermi surface. This theory has experimental support beyond the specific heat measurements. In particular which band is responsible for the superconductivity has been addressed experimentally by Riseman *et al.* using small angle neutron scattering [13]. For the superconducting state with the two component order parameter described above it has been predicted that a square vortex lattice is expected to occur when the field is applied along the  $c$ -axis [14]. The orientation of the square vortex lattice depends upon which of the bands are involved in the superconductivity. Riseman *et al.* observed a square vortex lattice and its orientation implies that the  $xy$  sheet of the Fermi surface is superconducting [13]. Furthermore, the measured size of the penetration depth is consistent with pairing on the  $xy$  sheet of the Fermi surface but not consistent with pairing over the whole Fermi surface [13]. It is of interest to note as well that the measurements of Imai *et al.* indicate that only the spin susceptibility of the  $xy$  orbitals exhibits a significant increase with decreasing temperature [15].

In this paper the role of impurities on orbital dependent superconductivity will be considered within the Born approximation. A standard approach using a nodeless  $p$ -wave state does not explain the rapid increase in the residual density of states with impurity concentration as seen by Nishizaki [10]. For this reason Maki and Puchkaryov proposed that the impurities in  $\text{Sr}_2\text{RuO}_4$  are sufficiently strong scatterers that the unitarity limit of the impurity problem should be used [11]. The unitarity limit has also been argued to be relevant for heavy fermion systems [16,17] and for high

$T_c$  materials [18–21]. In the heavy fermion case this limit is plausible due to small Fermi temperature ( $\approx 10$  K) that occurs in these materials while for high- $T_c$  materials the filled  $d$ -shell of Zn impurities may justify the unitarity limit. However neither of these two plausibility arguments apply to  $\text{Sr}_2\text{RuO}_4$  so, while the unitarity limit cannot be ruled out, it is worthwhile considering the Born limit in more detail. Here it is shown that a more realistic treatment of the impurity scattering within the Born approximation and within the context of orbital dependent superconductivity can explain the experimental results. The key element is inter-band scattering in which a quasiparticle with even parity under  $\sigma_z$  is scattered to a quasiparticle state with odd-parity under  $\sigma_z$ . Such a scattering implies that reflection under  $\sigma_z$  is locally broken by the impurity. This can occur for example if the impurity does not lie in the  $\text{RuO}_4$  plane, if it induces a rotation of the  $\text{RuO}_6$  octahedra about an in plane axis, or if there are layer stacking defects. After averaging over all impurity positions, this inter-band scattering does not mix the quasiparticle states of different parity, but does affect decrease the quasiparticle lifetimes. Here calculations of the specific heat as a function of temperature are performed to examine the consequences of this model and to compare to existing experimental data.

LDA band structure calculations of  $\text{Sr}_2\text{RuO}_4$  [22,23] reveal that the density of states near the Fermi surface is due mainly to the four Ru  $4d$  electrons in the  $t_{2g}$  orbitals. There is a strong hybridization of these orbitals with the O  $2p$  orbitals giving rise to antibonding  $\pi^*$  bands. The resulting bands have three quasi-2D Fermi surface sheets labeled  $\alpha, \beta$ , and  $\gamma$  (see Ref. [24]). In the planar limit due to the different parity under reflection ( $z \rightarrow -z$ ) the  $\alpha$  and  $\beta$  sheets consist solely of  $\{xz, yz\}$  Wannier functions and the  $\gamma$  sheet of  $xy$  Wannier functions. I assume an impurity potential that obeys the symmetry relation  $V(\mathbf{r}) = V(\sigma_z \mathbf{r})$  where  $\sigma_z$  is reflection through the  $\text{Ru}_2\text{O}_4$  plane and  $r_z = 0$  lies in the  $\text{Ru}_2\text{O}_4$  plane. On average such an impurity potential will not mix single particle excitations corresponding to different parity under  $\sigma_z$ . However the single particle excitations on each sheet will have two contributions to the lifetime: one from eigenstates of the same parity (intra-band) and one from eigenstates of opposite parity (inter-band) under  $\sigma_z$ . In the model considered below it will be assumed that the  $\alpha$  and  $\beta$  sheets are equivalent with respect to the single particle and superconducting properties. This is correct if a nearest neighbor tight binding dispersion is used to describe these sheets and is a reasonable approximation for more realistic dispersion relations. This leads to an effective two band model for the superconducting state in which the eigenstates of each band have opposite parity under  $\sigma_z$ . For simplicity two cylindrical Fermi surface sheets will be used: one with density of states equal to that of the  $\gamma$  sheet and one with density of states equal to that of the  $\alpha$  and  $\beta$  sheets (based on the measurements of Ref. [24] I take  $N_\gamma : (N_\alpha + N_\beta)$  to be 0.55 : 0.45). The interaction leading to superconductivity is taken to have the form

$$V_{l,l'}(\mathbf{k}, \mathbf{k}') = V_{l,l'} \frac{\mathbf{k} \cdot \mathbf{k}'}{k_{F_l} k_{F_{l'}}} \quad (1)$$

where  $k_{F_l}$  is the magnitude of the Fermi wavevector on sheet  $l$ . The gap matrix on each sheet is then of the form

$$\hat{\Delta}(l, \mathbf{k}) = \begin{pmatrix} 0 & c_l(k_x + ik_y)/k_{F_l} \\ c_l(k_x + ik_y)/k_{F_l} & 0 \end{pmatrix}. \quad (2)$$

Only the  $s$ -wave scattering potential is included and the  $s$ -wave scattering between band  $l$  and  $l'$  is characterized by  $u_{l,l'}$ . The resulting gap and self-energy equations are

$$c_l = T\pi \sum_{l',n} \frac{\tilde{V}_{l,l'} c_{l'}}{\sqrt{\tilde{w}_{n,l'}^2 + c_{l'}^2}} \quad (3)$$

and

$$\tilde{w}_{n,l} = w_n + \sum_{l'} \frac{\Gamma_{l,l'} \tilde{w}_{n,l'}}{\sqrt{\tilde{w}_{n,l'}^2 + c_{l'}^2}} \quad (4)$$

where  $\tilde{V}_{l,l'} = N_{l'} V_{l,l'}$ ,  $\Gamma_{l,l'} = \pi n_i N_{l'} [u_{l,l'}]^2$ ,  $N_l$  is the normal density of states on sheet  $l$ , and  $n_i$  is the concentration of impurities. Note that due to the odd-parity symmetry of the order parameter there is no re-normalization of the gap, consequently strong inter-band scattering does not lead to a state with an equal gap over the whole Fermi surface as is the case in  $s$ -wave superconductors [25,26]. This is partially a consequence of keeping only the  $s$ -wave Born scattering amplitude. If anisotropic contributions to the inter-band scattering amplitude are also included then in principle these terms will induce a gap on the  $\{\alpha, \beta\}$  sheets of the Fermi surface (if none exists in the clean limit). However this induced gap is subject to pair breaking due to the  $s$ -wave scattering amplitudes. This indicates that provided the anisotropic scattering amplitude is not too large keeping only the  $s$ -wave scattering amplitudes will capture the

underlying physics of  $\text{Sr}_2\text{RuO}_4$  (see References [27,28] for a discussion of physical consequences of anisotropic impurity potentials).

The equation for  $T_c$  deviates slightly from the standard Abrikosov-Gor'kov form and is given by

$$\ln(T_c/T_c^0) = f_+ - \frac{\sqrt{(V_{11}-V_{22})^2+4V_{12}V_{21}}}{2(V_{11}V_{22}-V_{12}V_{21})} \quad (5)$$

$$+ \frac{\sqrt{(V_{11}+V_{22})^2-4[1-f_-^2(V_{11}V_{22}+V_{12}V_{21})-f_-(V_{11}-V_{22})](V_{11}V_{22}-V_{12}V_{21})}}{2(V_{11}V_{22}-V_{12}V_{21})} \quad (6)$$

where  $f_+ = [\Psi(\frac{1}{2} + \rho_1) + \Psi(\frac{1}{2} + \rho_2)]/2 - \Psi(\frac{1}{2})$ ,  $f_- = [\Psi(\frac{1}{2} + \rho_1) - \Psi(\frac{1}{2} + \rho_2)]/2$ ,  $\Psi(x)$  is the digamma function,  $\rho_i = (\Gamma_{i1} + \Gamma_{i2})/(2\pi T_c)$ , and  $T_c^0$  is the transition temperature in the presence of no impurities.

The density of states (DOS) is given by

$$N(w) = -\frac{1}{\pi} \sum_l \int \frac{d^2k}{(2\pi)^2} \Im[G_l(k, z)|_{z=w+i\delta}] \quad (7)$$

$$= \sum_l N_l \sum_{l'} [\Gamma^{-1}]_{l,l'} \Im(\tilde{z}_{l'}) \quad (8)$$

It is of interest to determine  $N(w=0)$  in the limit of zero temperature as this quantity is measurable as the residual DOS in specific heat measurements. To date there has been no experimental evidence for a gap appearing on the  $\alpha$  and  $\beta$  sheets of the Fermi surface in  $\text{Sr}_2\text{RuO}_4$ . In view of this I consider initially the limit  $c_2 = 0$ . In Fig. 1 the residual DOS is plotted as a function of the transition temperature for the strong inter-band and intra-band scattering limits. Also shown in this Figure is the extrapolation from  $T = 0.3$  K of the same quantity from the data of Nishizaki *et al.* [10] (in Fig. 1  $T_c^0$  has been assumed to be 1.5 K). While a detailed comparison to the experimental data will require measurements at lower temperature it is clear that the intra-band scattering limit cannot account for the data. This indicates that inter-band scattering cannot be neglected. Note that in the limit  $\Gamma_{ii} = 0$  and  $c_2 = 0$  the density of states can be found analytically:

$$N_1(w) = \frac{w \sqrt{\sqrt{(c_1^2 + \Gamma_{12}^2 - w^2)^2 + 4\Gamma_{12}^2 w^2} + w^2 - c_1^2 - \Gamma_{12}^2} + \Gamma_{12} \sqrt{\sqrt{(c_1^2 + \Gamma_{12}^2 - w^2)^2 + 4\Gamma_{12}^2 w^2} + c_1^2 + \Gamma_{12}^2 - w^2}}{\sqrt{2} \sqrt{(c_1^2 + \Gamma_{12}^2 - w^2)^2 + 4\Gamma_{12}^2 w^2}} \quad (9)$$

In the zero frequency limit  $N(0) = N_2 + \frac{\Gamma_{12}}{\sqrt{c_1^2 + \Gamma_{12}^2}}$  showing that inter-band scattering increases  $N(0)$  from  $N_2$  for infinitesimal  $\Gamma_{12}$  which gives rise to the residual DOS seen in Fig. 1 Also shown in Fig. 1 is the residual density of states when  $c_2 = c_1/10$  in the strong inter-band scattering limit.

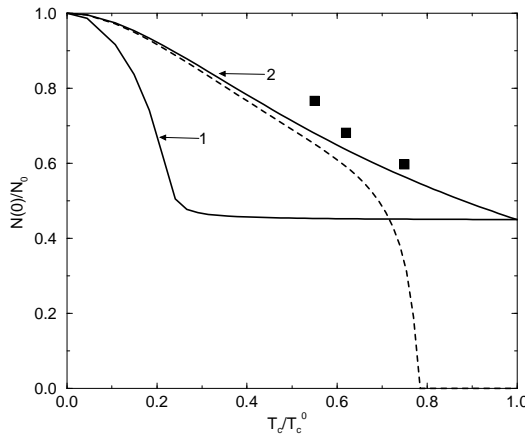


FIG. 1. Residual density of states for different impurity concentrations. The curve labeled 1 (2) is in the strong intra-band (inter-band) scattering limit and the experimental estimates are shown as squares. The dotted curve is in the strong inter-band scattering limit when the gap on the  $\{\alpha, \beta\}$  sheets is one tenth that of the  $\gamma$  sheet.

The specific heat is calculated by numerically evaluating the temperature derivative of the entropy. The entropy is given by

$$S = \int_0^{\epsilon_c} d\epsilon N(\epsilon) \{ [1 - f(\epsilon)] \ln[1 - f(\epsilon)] + f(\epsilon) \ln f(\epsilon) \}. \quad (10)$$

where  $\epsilon_c$  is the cut-off energy for the BCS interaction and  $f(\epsilon)$  is the Fermi distribution function. In Fig. 2 the results for  $C/T$  are shown for the intra-band scattering limit ( $u_{11} = u_{22} = 10u_{12}$ ) and the inter-band scattering limit ( $u_{11} = u_{22} = u_{12}/10$ ) in the limit  $V_{11} = 10V_{12}$  and  $V_{22} = 0$ .

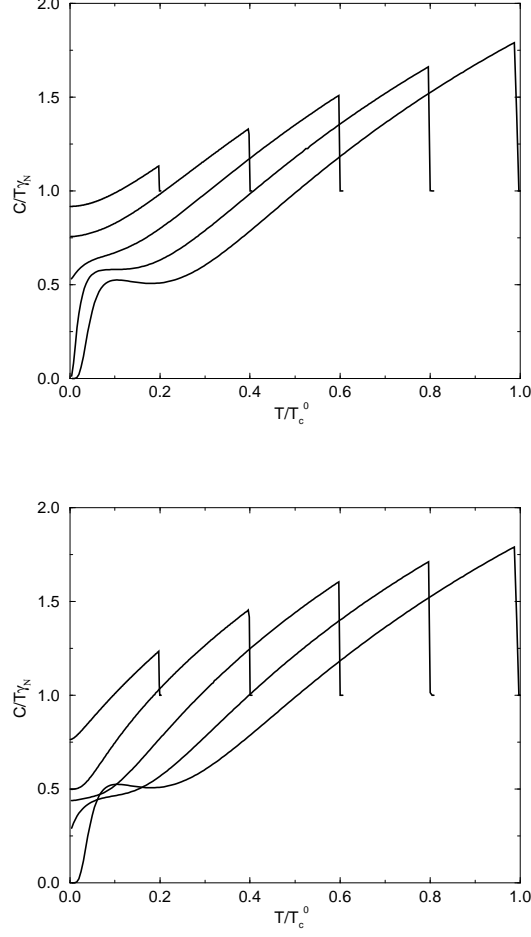


FIG. 2. Evolution of the  $C/T$  with increasing impurity concentration. The top (bottom) Figure is in the the strong intra-band (inter-band) scattering limit.

Fig. 2 shows that inter-band scattering raises the apparent residual DOS (*i.e.* that found by using entropy balance to extrapolate from measurements taken down to  $T = T_c^0/5$ ) and decreases the specific heat jump relative to intra-band scattering. Also any gap on the  $\{\alpha, \beta\}$  bands will be less rapidly destroyed by inter-band scattering than by intra-band scattering.

A theory of impurities within the context of orbital dependent superconductivity has been developed for  $\text{Sr}_2\text{RuO}_4$ . In contrast to known results for nodeless  $p$ -wave superconductors, a strong dependence of the low temperature behavior of the specific heat on impurity concentration is shown to be a consequence of this theory in the Born approximation. This behavior is due to the impurity scattering between bands of opposite parity symmetry under reflection through the  $\text{RuO}_4$  plane. This theory accounts for the recent measurements of the specific heat for different impurity concentrations provided this inter-band scattering is not neglected.

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- [1] Y. Maeno, H. Hashimoto, K. Yoshida, S. Nishizaki, T. Fujita, J.G. Bednorz, and F. Lichtenberg, *Nature* **372**, 532 (1994).
- [2] T.M. Rice and M. Sigrist, *J. Phys.: Condens. Matter* **7**, L643 (1995).
- [3] K. Ishida, Y. Kitaoka, K. Asayama, S. Ikeda, and T. Fujita, *Phys. Rev. B* **56**, 505 (1997).
- [4] R. Jin, Y. Zadorozhny, Y. Liu, D.G. Schlom, Y. Mori, and Y. Maeno, *Phys. Rev. B* in press.
- [5] A.P. Mackenzie, R.K.W. Haselwimmer, A.W. Tyler, G.G. Lonzarich, Y. Mori, S. Nishizaki, and Y. Maeno, *Phys. Rev. Lett.* **80**, 161 (1998).
- [6] G.M. Luke, Y. Fudamoto, K.M. Kojima, M.I. Larkin, J. Merrin, B. Nachumi, Y.J. Uemura, Y. Maeno, Z.Q. Mao, Y. Mori, H. Nakamura, and M. Sigrist, *Nature* **394**, 558 (1998).
- [7] K. Ishida, H. Mukuda, Y. Kitaoka, K. Asayama, Z.Q. Mao, Y. Mori, and Y. Maeno, *Nature* **396**, 658 (1998).
- [8] L.P. Gor'kov and P.A. Kalugin, *Pis'ma Zh. Eksp. Teor. Fiz.* **41**, 208 (1985) [*JEPT Lett.* **41**, 253 (1985)].
- [9] K. Ueda and T.M. Rice, *Theory of Heavy Fermions and Valence Fluctuations*, edited by T. Kasuya and T. Saso (Springer, Berlin), 267 (1985).
- [10] S. Nishizaki, Y. Maeno, S. Farner, S. Ikeda, and T. Fujita, *J. Phys. Soc. Jpn.* **67**, 560 (1998).
- [11] K. Maki and E. Puchkaryov, *Europhys. Lett.* **45**, 263 (1999).
- [12] D.F. Agterberg, T.M. Rice, and M. Sigrist, *Phys. Rev. Lett.* **78**, 3374 (1997).
- [13] T.M. Riseman, P.G. Kealey, E.M. Forgan, A.P. Mackenzie, L.M. Galvin, A.W. Tyler, S.L. Lee, C. Ager, D. McK. Paul, C.M. Aegerter, R. Cubitt, Z.Q. Mao, S. Akima, and Y. Maeno, *Nature* **396**, 242 (1998).
- [14] D.F. Agterberg, *Phys. Rev. Lett.* **80**, 5184 (1998).
- [15] T. Imai, A.W. Hunt, K.R. Thurber, and F.C. Chou, *Phys. Rev. Lett.* **81**, 3006 (1998).
- [16] S. Schmitt-Rink, K. Miyake, and C. Varma, *Phys. Rev. Lett.* **57**, 2575 (1986).
- [17] P. Hirschfeld, D. Vollhardt, and P. Wolffe, *Solid State Commun.* **59**, 111 (1986).
- [18] P.J. Hirschfeld and N. Goldenfeld, *Phys. Rev. B* **48**, 4219 (1993).
- [19] T. Hotta, *J. Phys. Soc. Jpn.* **62**, 274 (1993).
- [20] Y. Sun and K. Maki, *Phys. Rev. B* **51**, 6059 (1995).
- [21] T. Hotta, *Phys. Rev. B* **52**, 13041 (1995).
- [22] T. Oguchi, *Phys. Rev. B* **51**, 1385 (1995).
- [23] D.J. Singh, *Phys. Rev. B* **52**, 1358 (1995).
- [24] A.P. Mackenzie, S.R. Julian, A.J. Diver, G.G. Lonzarich, Y. Maeno, S. Nishizaki, and T. Fujita, *Phys. Rev. Lett.* **76**, 3786 (1996).
- [25] A.A. Golubov and I.I. Mazin, *Phys. Rev. B* **55**, 15146 (1997).
- [26] N. Schopohl and K. Scarnberg, *Solid State Commun.* **22**, 371 (1977).
- [27] S. Haas, A.V. Balatsky, M. Sigrist, and T.M. Rice, *Phys. Rev. B* **56**, 5108 (1997).
- [28] G. Haran and A.D.S. Nagi, *Phys. Rev. B* **58**, 12 441 (1998).